SHIGINA, K. K.

Shigina, K. K.

"Investigation of the corrosion aggressiveness of crankcase oils and its effect on the wear of the bearings of tractor diesel engines." min Higher Education UssR. Moscow Inst of the Mechanization and Electrification of Agriculture imeni V. M. Molotov. Moscow, 1956. (Dissertation for the Degree of Candidate in Technical Sciences).

Knizhnaya letopis'
No. 25, 1956. Moscow.

SHIGINA, R.K., kand.tekhn.nauk

Improve the system of lubricating construction equipment. Stroi. i dor mash. 7 no.6:11-13 Je '62. (MIRA 15:7)
(Construction equipment--Maintenance and repair)
(Lubrication and lubricants)

GEFTER, V.A., LEVITANSKAYA, P.B., SHIGINA, Ye.A.

A new method for detecting helminthova in dust collected from household articles with a vacuum cleaner [with summary in English]. Med. paraz. i paraz. bol. 27 no.2:173-176 Mr-Ap '58 (MIRA 11:5)

1. Iz sanitarno-epidemiologicheskoy stantsii Moskovskoy okruzhnoy zheleznoy dorogi (nach. stantsii I.I. Mogilevskiy)
(HELMINTHS,
ova, isolation from household dust collected by vacuum cleaner (Rus))

VID MA, ZH.A.; [illegible]

Using unfired runner brick. Ogneupory 25 no.12:556-560 '60.
(MIRA 14:1)

1. Nizhne-Tagil'skiy metallurgicheskiy kombinat.
(Firebrick--Testing)

GEFTER, V.A.; SHIGINA, Ye.A.

Improvement of the method of sanitary helminthological examination of soils. Med. paraz. i paraz. bol. 31 no.6: 742-744 N-D '62. (MIRA 17:11)

1. Iz parazitologicheskogo otdeleniya sanitarno-epidemiologicheskoy stantsii Moskovsko-okruzhnogo otdeleniya Moskovskoy zheleznoy dorogi (nachal'nik I.I. Mogilevskiy).

36907 I prabserov, A. V. Vliyaaniye zasukhi na rost i razvitiye sel'skokhozyaystvennykh (Zernovykh) Kul'tur. Trudy Tsentr. In-ta prognozov, vyp. 13, 1949, c. 67-82

SO: LETOPIS' NO. 37, 1949

SHIGOLEV, A.A.

530 /Rukovodstvo dlya sostavleniya Fenologicheskikh prognozov/. Oves. yachmen' i len. Pod red. I.M. Petunina. L., Gidrometeoizdat, 1954. 24 s. s ill. 22sm. (Glav. upr. gidrometerol. Sluzhby pri sovete ministrov SSSR. Tsentr. in-t prognozov. Metod. ukazaniya. Vyp. 25 S. -kh. meteorologiya). 2,000ekz. Bespl. --Na tit. L. zagl: Dopolneniye k «Rukovodstvu dlya sostavleniya fenologicheskikh prognozov .--- Na obc. tol'ko zagl. serii. --[54-13403 zh] 63: 551.5+577.49

SO: Knizhnaya Letopis, Vol. 1, 1955

USSR/Cultivated Plants. Grains. M

Abs Jour: Ref Zhur-Biol., No 5, 1958, 20274.

Author : A.A. Shigolev
Inst : Central Forecasting Institute.
Title : Determining the Thermal Indices for the Rate of Growth of Corn. (Ob opredelenii termicheskikh pokazateley skorosti razvitiya kukuruzy).

Orig Pub: Tr. Tsentr. in-ta prognozov, 1956, vyp. 47 (74), 51-58.

Abstract: The duration of the phenological phases of corn depends to a high degree on the surrounding temperature. The period from the formation of shoots to that of staminate flowers in the Krasnodarskiy 1/49 Hybrid variety lasted 20 days longer in Moscow than in Krasnodar. The total of the temperatures in effect during this period was nearly equal (794 and 803), despite the differences in

Card : 1/2

USSR/Cultivated Plants. Grains.

Abs Jour: Ref Zhur-Biol., No 5, 1958, 20274.

the duration of daily lighting. The sum of temperatures in effect for the period from the opening of blossoms to milky ripeness (as well as from milky to waxy ripenesses) was a constant value for the variety. These sums naturally ran to 379 and 297 for the 1/49 Krasnodarskiy Hybrid with insignificant variations according to the points of observation. The natural laws indicated by the 1/49 Krasnodarskiy Hybrid were backed up in other varieties of corn as well (the Liming Krasnodarskiy, Sterling, Bessarabskaya, North Dakotan, Khar'kovsaya 23, the Dnepropetrovskiy Hybrid). One may assume 6^{o} as the lower limit of effective temperature during the entire period of corn vegetation.

Card : 2/2

SHIGOLEV, A.A.

Temperature as a quantitative agricultural and meteorological indicator of the rate of development of plants and some elements of their productivity. Trudy TSIP no.53:75-81 '57. (MLRA 10:8)
(Plants, Effect of temperature on)

SHIGOLEV, A.A.; PONOMAREV, B.P.

Relationship between the number of spikelets in the ear of spring wheat and agrometeorological conditions. Trudy TSIP no.72:3-11 '58. (MIRA 12:1)

(Wheat) (Meteorology, Agricultural)

SHIGOLEV, A.A., otv. red.

[Seasonal development of nature in the central provinces of the R.S.F.S.R. in 1959] Sezonnoe razvitie prirody tsentral'nykh oblastei RSFSR, 1959.g. Leningrad, 1961. 38 p. (MIRA 15:7)

1. Geograficheskoye obshchestvo SSSR. Moskovskiy filial.
(Phenology)

SHIGOLEV, A.A.

"From work practices in a critical analysis of phenological data of agricultural yearbooks" by G.Z.Ventskevich. Reviewed by A.A.Shigolev. Meteor. i gidrol. no.3:58-60 Mr '62. (MIRA 15:3)

(Phenology) (Ventskevich, G.Z.)

SHIGOLEV, PV

7738 AERE-Lib/Trans-671
EFFECTS OF ELECTROPOLISHING ON THE PHYSICAL CHEMICAL PROPERTIES OF THE SURFACE OF PURE ALUMINUM. P. V. Schigolev. Translated by T. Turton from Zhur. Fiz. Khim. 29, 682-4(1955). 6p.

It is established that electropolishing considerably increases the coefficient of reflection of light of the aluminium (on the average by 12 to 15%). Electromicroscopic investigation showed that the micro-relief of the surface of the electropolished aluminium is not perfect. A cellular structure appears on the surface, apparently caused by unequal melting, and as a result a new microroughness appears which may be observed on high magnification (x 18000). Electropolishing causes a considerable increase in electrical resistance of the surface of aluminium. The potential of puncturing of the film on the surface of electropolished aluminium is about 25 times higher than the potential of puncturing of the natural film formed on the surface of sheet aluminium in the process of production and further storage. On the X-radiograms of the surface of electropolished aluminium, were discovered, besides the basic lines of aluminium, new lines which apparently belong to some unknown modification of Al_2O_3. (auth)

Metals 1

Df

RYABOV, Vasiliy Sergeyevich, podpolkovnik; SHIGOREV, P.A., polkovnik, red.; MEZHERITSKAYA, N.P., tekhn.red.

[Honor and dignity of the Soviet soldier] Chest' i dostoinstvo sovetskogo voina. Moskva, Voen.izd-vo M-va obor. SSSR, 1957. 84 p. (MIRA 11:5)

(Russia--Armed forces)

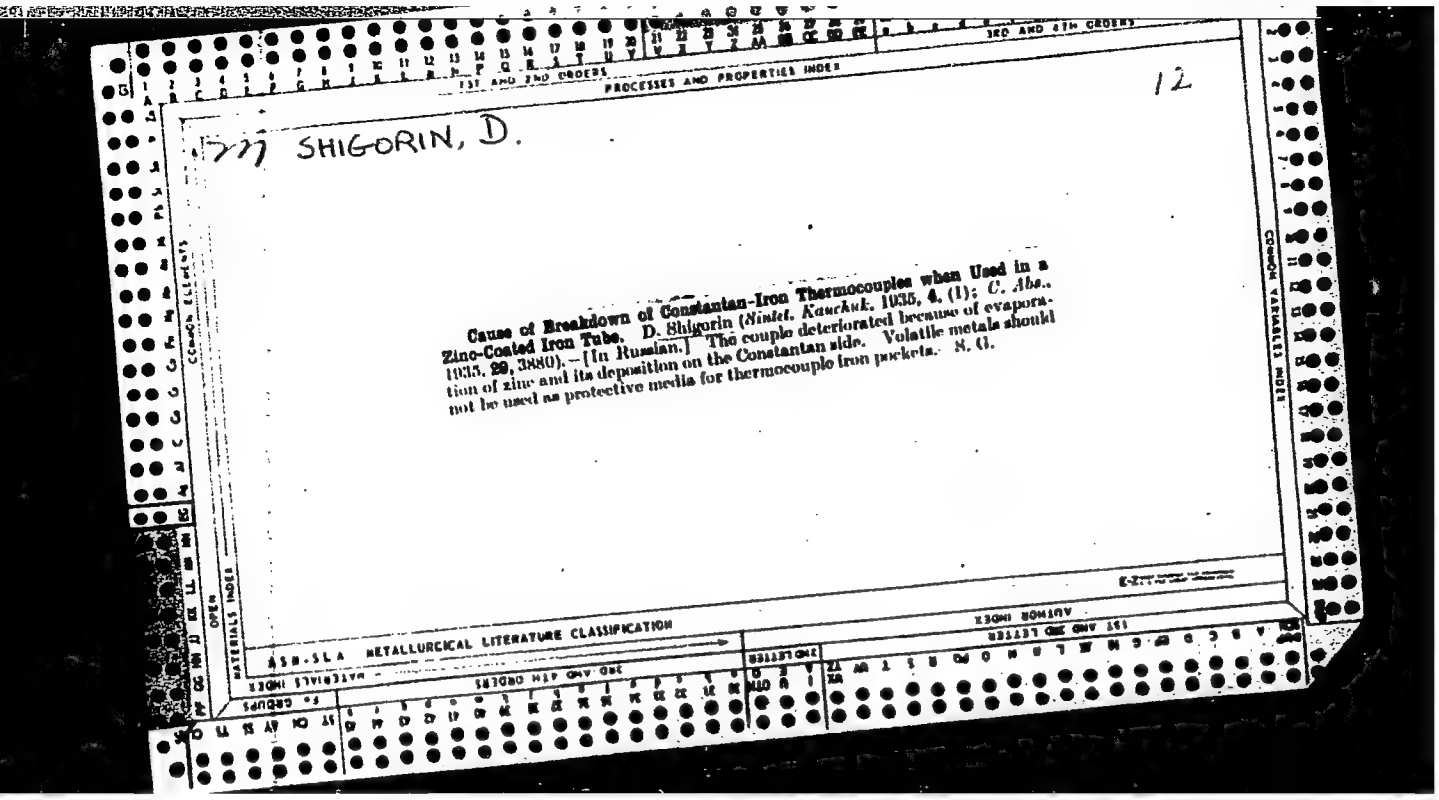
SHIGOREV, P.

Highest rewards of the society. Kryl.rod. 12 no.9:17-18 S '61.
(MIRA 14:9)
(Aeronautical societies--Competitions)

Shigorev P.A.

BORISOV, B.A., YEGOROV, N.S.; KOZEV, A.I.; SHIGOREV, P.A., polkovnik, red.; KONOVALOVA, Ye.K., tekhn.red.

[Outstanding members of the Soviet Army and Navy] Otlichniki Sovetskoi Armii i Voenno-Morskogo Flota. Moskva, Voen. izd-vo M-va oborony SSSR, 1957. 207 p. (MIRA 10:12)
(Russia--Army) (Russia--Navy)



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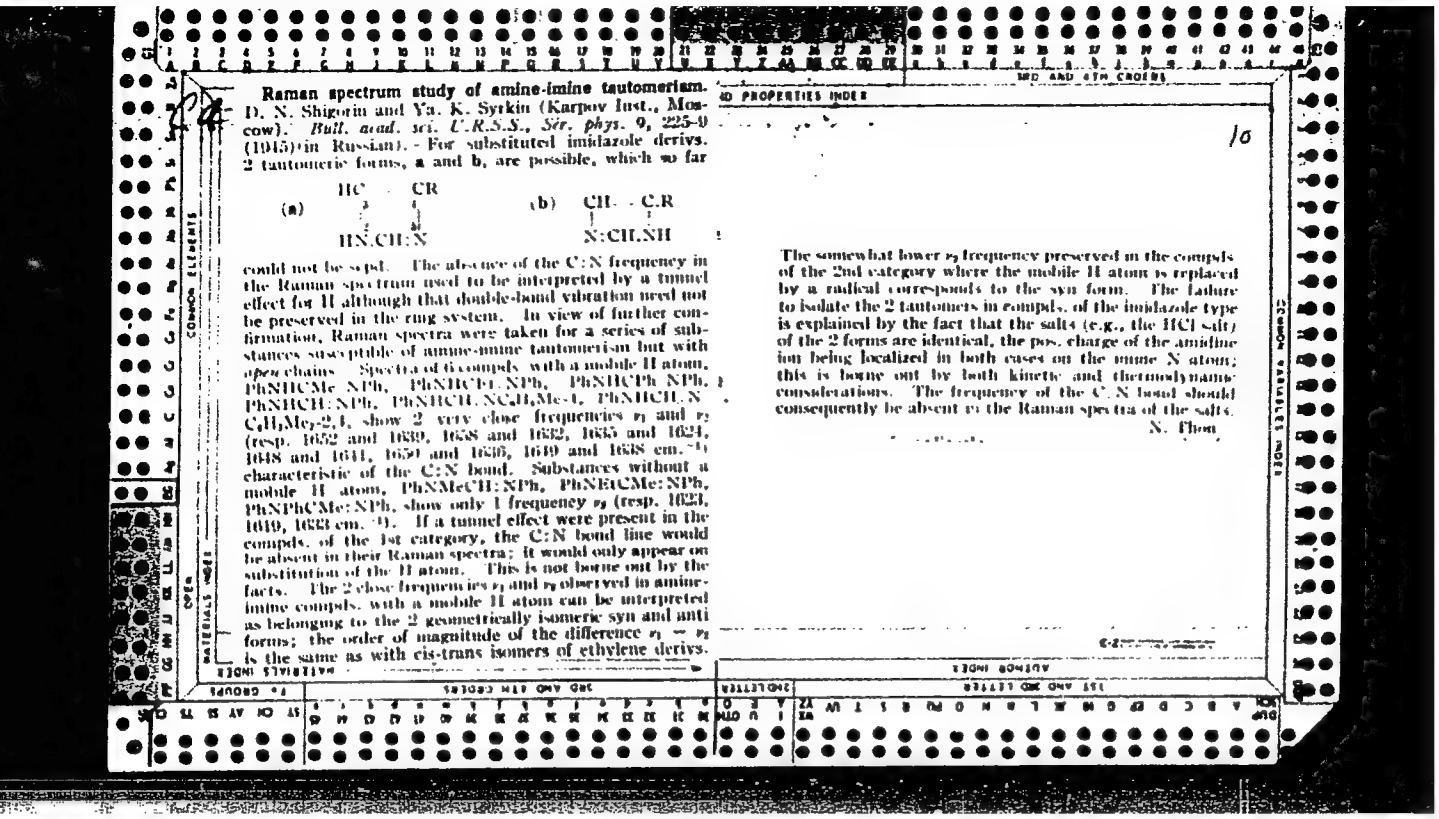
SHIGORIN, D.

Cause of Breakdown of Constantan-Iron Thermocouples when Used in a Zinc-Coated Iron Tube. D. Shigorin (*Nizhet. Kauchuk*, 1935, 4, (1); *C. Abs.*, 1935, 29, 3880). — [In Russian.] The couple deteriorated because of evaporation of zinc and its deposition on the Constantan side. Volatile metals should not be used as protective media for thermocouple iron pockets. S. G.



Raman spectrum study of amine-imine tautomerism. D. N. Shigorin and Ya. K. Syrkin (Karpov Inst., Moscow). *Bull. acad. sci. U.R.S.S., Sér. phys.* 9, 225-9 (1945)(in Russian). - For substituted imidazole derivs. 2 tautomeric forms, a and b, are possible, which so far

(a) HC–CR / HN.CH:N (b) CH–C.R / N:CH.NH

could not be separ. The absence of the C:N frequency in the Raman spectrum used to be interpreted by a tunnel effect for H although that double-bond vibration need not be preserved in the ring system. In view of further confirmation, Raman spectra were taken for a series of substances susceptible of amine-imine tautomerism but with *open* chains. Spectra of 6 compds. with a mobile H atom, PhNHCMe:NPh, PhNHCH:NPh, PhNHCPh:NPh, PhNHCH:NPh, PhNHCH:NC$_6$H$_4$Me-4, PhNHCH:N·C$_6$H$_3$Me$_2$-2,4, show 2 very close frequencies ν_1 and ν_2 (resp. 1652 and 1639, 1658 and 1632, 1655 and 1624, 1648 and 1641, 1650 and 1636, 1649 and 1638 cm.$^{-1}$) characteristic of the C:N bond. Substances without a mobile H atom, PhNMeCH:NPh, PhNEtCMe:NPh, PhNPhCMe:NPh, show only 1 frequency ν_3 (resp. 1623, 1619, 1633 cm.$^{-1}$). If a tunnel effect were present in the compds. of the 1st category, the C:N bond line would be absent in their Raman spectra; it would only appear on substitution of the H atom. This is not borne out by the facts. The 2 close frequencies ν_1 and ν_2 observed in amine-imine compds. with a mobile H atom can be interpreted as belonging to the 2 geometrically isomeric syn and anti forms; the order of magnitude of the difference $\nu_1 - \nu_2$ is the same as with cis-trans isomers of ethylene derivs.

The somewhat lower ν_2 frequency preserved in the compds of the 2nd category where the mobile H atom is replaced by a radical corresponds to the syn form. The failure to isolate the 2 tautomers in compds. of the imidazole type is explained by the fact that the salts (e.g., the HCl salt) of the 2 forms are identical, the pos. charge of the amidine ion being localized in both cases on the imine N atom; this is borne out by both kinetic and thermodynamic considerations. The frequency of the C:N band should consequently be absent in the Raman spectra of the salts.

N. Thon.

L 62934-65 EWT(l)/EWT(m)/EWP(j) IJP(c) RM

ACCESSION NR: AR5012283 UR/0058/65/000/003/D074/D074

27
13

SOURCE: Ref. zh. Fizika, Abs. 3D597

AUTHOR: Shcheglova, N. A.; Shigorin, D. I.

TITLE: Quasi-line luminescence spectra of aromatic diketones at 77°K

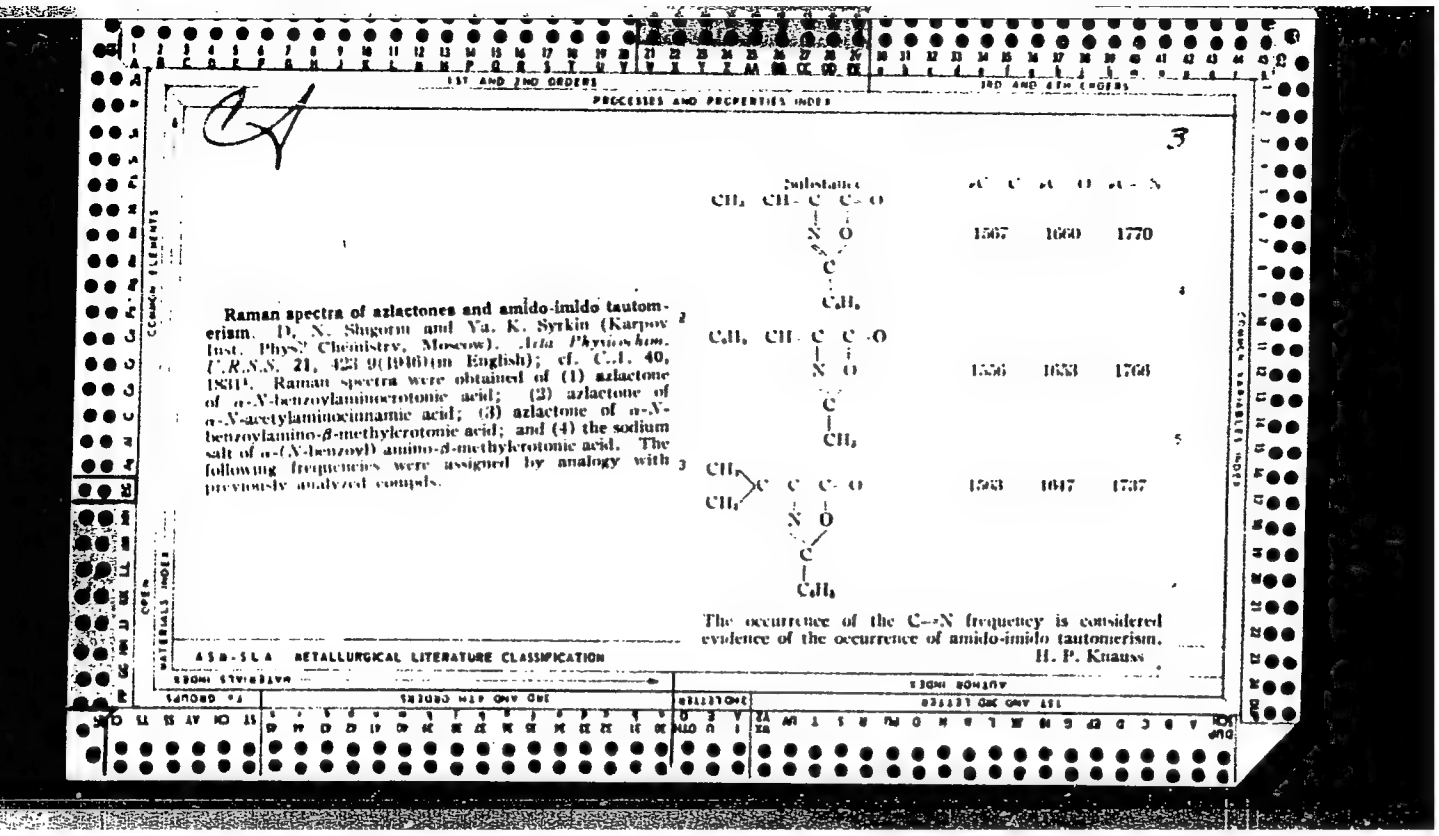
CITED SOURCE: Tr. Komis. po spektroskopii, AN SSSR, vyp. 1, 1964, 648-661

TOPIC TAGS: aromatic ketone, electron structure, electron energy level, line spectrum, luminescence spectrum, electron transition

TRANSLATION: Quasi-line luminescence spectra of aromatic diketones are studied. A vibrational analysis of the spectra is given; the nature of the electron transitions is determined and the positions of the electron levels are found. The effect of substituents on the emission and absorption spectra is examined.

SUB CODE: NP, GC ENCL: 00

Card 1/1



PROCESSES AND PROPERTIES INDEX

3

Raman spectra of azlactones and amido-imido tautomerism. D. N. Shigorin and Ya. K. Syrkin (Karpov Inst. Phys. Chemistry, Moscow). *Acta Physiochim. U.R.S.S.* **21**, 423-9(1946)(in English); cf. C.A. **40**, 1831⁹. Raman spectra were obtained of (1) azlactone of α-*N*-benzoylaminocrotonic acid; (2) azlactone of α-*N*-acetylaminocinnamic acid; (3) azlactone of α-*N*-benzoylamino-β-methylcrotonic acid; and (4) the sodium salt of α-(*N*-benzoyl) amino-β-methylcrotonic acid. The following frequencies were assigned by analogy with previously analyzed compds.

Substance			
	1567	1660	1770
	1556	1653	1766
	1563	1647	1737

The occurrence of the C=N frequency is considered evidence of the occurrence of amido-imido tautomerism.

H. P. Knauss

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

SHIGORIN, D. N. PA19/49T5

USSR/Chemistry - 2, 4-Pentanedione Sep/Oct 48
Chemistry - Spectra, Infrared

"Optic Studies of the Hydrogen Bond of Acetyl-acetone and Its Derivatives," D. N. Shigorin, 3/4 p

"Iz Ak Nauk SSSR, Ser Fiz" Vol XII, No 5

Investigates infrared absorption and combination dispersion spectra of acetyl-acetone and some of its derivatives (Synopsis. Paper will be printed in full in "Zhur Fiz Khimii.")

[redacted] 19/49T5

SHIGORIN, D. N.

[redacted]

PA 38/49T2

USSR/Chemistry - Amidines Mar 49
Chemistry - Spectra, Vibrational

"Vibration Spectra of Amidines," D. N. Shigorin, Ya. K. Syrkin, Physicochem Inst imeni L. Ya. Karkov, Moscow, 10 pp

"Zhur Fiz Khimii" Vol XXIII, No 3

Studies combination dispersion spectra and infrared spectra of 13 amidines. Frequency C=N is characteristic, and fluctuates from 1,604 to 1,676 cm-1. Amidines are associated due, to presence of hydrogen bonds and apparently association is either of the chain or ring type.

38/49T2

[redacted]

USSR/Chemistry - Amidines (Contd) Mar 49

Hydrogen bond N-H with nitrogen imine is, apparently, more strongly expressed than with nitrogen amine. Shows that fatty amidines of type NN'-diethylacetamidine are strongly associated, but aromatic ones of type NN'-diphenylacetamidine are weakly associated. Submitted 16 Jun 48.

38/49T2

SHIGORIN, L. N.

**TT.177 (Optical investigation of the hydrogen bond of acetylacetone and its derivatives) Opticheskoe issledovanie vodorodnoi svjazi atsetilatsetona i ego proizvodnykh.
SO: Zhurnal Fizicheskoi Khimii, 23(5): 505-515, 1949

SHIGORIN, D. N.

Shigorin, D. N. Intesity of ban spectra for double bond linkage in acetoacetic ester and acetyl-aceton in connection with their structure. Pages 395 - 400.

SO: Bulletin of the Academy of Sciences, Izvestia, (USSR) Vol. 14, No. 4 (1950) Series on Physics.

(A

Optical investigation of keto-enol tautomerism in cyclic systems. D. N. Shigorin (Karpov Phys.-Chem. Inst., Moscow). *Zhur. Fiz. Khim.* 24, 924-31(1950).—The vibrational spectra of the keto-enolic systems in Et 2-oxocyclohexane-1-carboxylate (I) and the corresponding cyclopentane ester (II) were investigated. With I, the equil. amt. of the enolic form was 85–90%; with II, the equil. amt. of the enolic form was only 5–7%. An intramol. H bond is formed preferentially in the enolic form of I; the OH group, which participates in the formation of the H bond, was characterized in the infrared region by a displaced and erased band at about 3150 cm.$^{-1}$. With II there is an intermol. H linkage formed between the OH enolic form and the C:O keto form. In a 1:10 C_6H_{14} soln., an intramol. H linkage is formed which is changed but little by interaction with the nonpolar solvent. When pyridine was used as the solvent for I and II (1:10) instead of the H linkage, O—H...O, there arises O—H...N. In this case the OH group has a frequency of 3300–70 cm.$^{-1}$. P. W. Howerton

CA 10

Optical investigation of the hydrogen bonds in acetoacetic ester. D. N. Shigorin (Karpov Phys.-Chem. Inst., Moscow). *Zhur. Fiz. Khim.* 24, 932-7(1950).—The vibrational spectrum of the OH group in the enolic form of $AcCH_2CO_2Et$ was investigated. In the liquid state, an intermol. bond between the keto and enol forms is preferential, but in inert solvents (C_6H_{12}, CCl_4, CS_2) at low concn. (1:10 and lower) an intramol. H bond is formed in the enolic form. The formation of this bond is accompanied by a rapid displacement of the tautomeric equil. toward the formation of the enolic form. Paul W. Howerton

CA

3

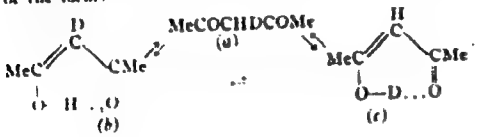
Vibration spectra of acetylacetone derivatives, acetoacetic ester, and the hydrogen bond. D. N. Shigorin and A. P. Skoldinov (Karpov Phys.-Chem. Inst., Moscow). *Zhur. Fiz. Khim.* 24, 955–67(1950).—Neither AcCH(R)Ac nor AcCH(R)CO_2Et as liquid or in an inert solvent forms an intramol. H bond. The bands of the OH group of enolic isomers are characterized at 3550–3000 cm.$^{-1}$.

Paul W. Howerton

CA

3

Raman spectra of deuterioacetylacetone and of deuterioacetoacetic acid ester. D. N. Shigorin and Yu. K. Syrkin. *Doklady Akad. Nauk S.S.S.R.* **70**, 1033-6 (1950).—MeCOCHDCOMe (I) and MeCOCHDCO$_2$Et (II) were synthesized by decompn. of the corresponding Cu salts with D_2SO_4. The Raman spectra, taken 24 hrs. after the synthesis, i.e. after the keto-enol equil. has been established, are (cm.$^{-1}$) (I) 2900(2), 2923(20), 2400($^1/_2$), 2300(3), 2233(1), 2172(2), 1720(3), 1652(2), 1600(1b), 1532(10), 1437(3), 1374(5), 1300($1^1/_2$b), 1246(5), 1170-($1^1/_2$b), 1082(0), 1037(3), 987($1^1/_2$), 925(3), 877(4), 836(2), 780(1), 636(10), 554(5), 505(4), 401($1^1/_2$), 224(4b); (II) 2980(4), 2930(20b), 2238(1), 2177(3), 1737(5), 1712(4), 1620(2), 1589(10), 1452(7), 1340($1^1/_2$), 1163(3), 1110(0b), 1035(3b), 934($1^1/_2$b), 808(4b), 865(4b), 798(2b), 757(2b), 732(4b), 627(4b), 594(4), 540(3), 525(2). The Raman spectrum permits an estn. of the forms



in equil. in I. The frequency of C=C is lowered when the C is bound with D. The frequency 1532 cm.$^{-1}$ evidently belongs to C=C in HOC=CD, and 1600 to C=C in DOC=CH. The ratio of the intensities indicates that the enol form with O—H is present in a much greater amt. than the enol with O—D. Similarly, in II, 1589 belongs to OHC=CD, and 1629 to DOC=CH, and the enol with O—H is more abundant than the enol with O—D. The ratio of enols ROH/ROD in I is about twice as great as in II, i.e., the equil. is more strongly shifted in favor of the mol. with light H in the case of stronger acid (enol I). In 1:10 solns. in CCl_4 and C_6H_{12}, the ratio ROH/ROD for I is about 3.5, as against 10 in the pure liquid; for II, that ratio is 5 in the pure liquid, 3.5 in soln. in CCl_4. In light MeCOCH$_2$COMe, the frequency 3075 is assigned to the valence vibration C—H in C=C—H; 1300 and 1246 are deformation vibrations of the CH_3 group of the keto form. In I, 3075 is absent, and there appears a frequency 2300, characteristic of the valence vibration C—D in C=C—D; the weakness of 1300 and of 1246 in I indicates absence of CH_3 which is replaced by CHD. In this group, the valence vibrations C—D have the frequencies 2233 and 2172; the frequency 1082 is assigned to deformation vibrations C—D. The very weak 2400 is apparently characteristic of O—D. The intensities of the frequencies belonging to O—H are practically the same in I and in light MeCOCH$_2$COMe. The same changes in the frequencies C—H and C—D are found also in II.

N. Thon

SHIGORIN, D. N.

USSR/Chemistry - Structural Theory Jun 51

"Some Problems of the Theory of Chemical Structure of Molecules," D. N. Shigorin

"Zhur Fiz Khim" Vol XXV, No 6, pp 737-752

Discusses structural theory from the viewpoint of opponents of resonance theory. In reference to conjugation of bonds, states that the mutual influence of atoms and groups in a mol determines the chem character of the mol. Every mol has bonds which are characteristic of the compd in question and different from those of mols of all other org compds. While current concepts are based on

206T17

USSR/Chemistry - Structural Theory (Contd) Jun 51

consideration of displacement of electrons along the chain and of the resulting polarity, changes in the type of movement of electrons are disregarded.

206T17

SHIGORIN, D. N.

USSR/Chemistry - Amidines and Imidoesters Jul 51

"Spectra of Combination Scattering of Light by Amidine and Imidoester Hydrochlorides," D. N. Shigorin, Phys Chem Inst imeni L. Ya. Karpov, Moscow

"Zhur Fiz Khim" Vol XXV, No 7, pp 798-802

Studied Raman spectra of hydrochlorides of several amidines and imidoesters. In these hydrochlorides frequency of C=N bond is strongly suppressed due to interaction of bond with other groups in mol. On basis of the obtained data, amidine structure is R-C(=$\overset{+}{N}H_2$)-$\overset{+}{N}H_2$.

206T21

SHIGORIN, D. N.

Bardyshev, I. I., Shorygin, P. P., Shigorin, D. N.- "Combination scattering spectra of some terpenes". (p. 568)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1952, Vol. 22, No. 4

SHIGORIN, D. N.

Discussion of some questions of chemical formation of molecules. II. D. N. Shigorin. *Zhur. Fiz. Khim.* 26, [illegible]. The law of quantum [illegible] of chem. valence, and the theory [illegible] TR must be restricted to a simple compd. [illegible] in applied to a complicated compd without [illegible]. The originality of the TR ignored the theory [illegible] formation of A. M. Butlerov. An example is the [illegible] of He and H. In contradiction of the Heitler-London theory Heil cannot exist, because the Pauli principle would be violated. On the other hand, the theory of pairing of electrons is not valid in complicated compds. According to Butlerov, with consideration of the wave-corpuscular nature of electrons, an electron participating in bond formation can act simultaneously in bond formation between 2 or more atoms not directly connected, owing to the motion in the field between nuclei. There are known cases where the no. of bonds between atoms is larger than the no. of valence electrons (e.g. borane), so phys. satn. of the atom does not correlate with the chem. satn. of the atom in the mol. In contradiction to quantum chemistry, not all centers are equal. Here must be taken into account the mutual interaction of π-electrons (πe) with σ-electrons, e.g. replacement of H in CH_2:CH_2 (I) by halogen. Lowering the dipole moment in CH_2:CHX can be attributed to the "effect of character change" of πe between C and X atoms. The C-X bond in this and similar mols. does not have the nature of pure σ- or π-bonds. As more H atoms are replaced by X or Ph, the C-C bond is weakened, owing to partial interaction of πe with X or Ph. If H in I or in C_2H_4 is replaced by a group that has a lower electron d., interaction of πe with $C^{+\sigma}$ should not be considered, e.g. CH_2:$CHCH_2X$, $PhCH_2X$, or CH_2:$CHCX_3$. This interaction of πe is supported by the spectral analysis of acetone (λ = 1684 cm.$^{-1}$ for the CO group should be 1708 cm.$^{-1}$). λ increases as more H is replaced by X (~17 cm.$^{-1}$ per each X). The effect of πe, of Ph in Ph_3COH, $PhONa$, and $PhCNa$, and in CH_2:$CHCH_3$, CH_2:$CHCH_2CH_2CH_3$, and CH_2:$CHCMe_2CMe_2CMe_3$ is discussed. Structural formulas indicating distribution of the electron d., spin, and charge are given.

Michael Dymicky

SHIGORIN, D. N.

PA 242T16

USSR/Chemistry - Molecular Structure Nov 52

"Certain Questions on the Chemical Structure of Molecules: III. (Answer to O. A. Reutov)," D. N. Shigorin

"Zhur Fiz Khim" Vol 26, No 11, pp 1681-1687

The author refers to O. A. Reutov's critical analysis of his work (in 1952). He criticizes him in turn for ignoring the work of A. M. Butlerov in his (Reutov's) own theories. The problem that concerns Shigorin most is the satn of chemical valences in complex org mols together with the problem of revealing the nature of the mutual

242T16

effect of atoms or groups in compds (especially compds with conjugated bonds). Shigorin disparages the work of Reutov, and explains his own conception of orientation in chlorobenzene. He criticizes Reutov's concept of the "joining of bonds" within a mol, and states that the effect of the mutual influence of atoms and groups in mols does not consist in the interaction of bonds, but in the interaction of electrons, depending on the energetic character of their movement and on the nature of the atoms and their mutual position.

242T16

SHIGORIN D. N.

PA 240T8

USSR/Chemistry - Synthetic Fibers Dec 52

"Investigation of the Physical Structure of Synthetic Polyamides by the Method of Oscillation Spectra," N. V. Mikhaylov, D. N. Shigorin and S. P. Makar'yeva, All-Union Sci Res Inst of Synthetic Fibers

"DAN SSSR" Vol 87, No 6, pp 1009-1012

The nature of bonds holding the fibers together in a polycaprolactam fiber were studied using infra-red absorption spectroscopy. Comparison of the results obtained from spectral analysis

240T8

with data on the mech properties of polycaprolactam confirm the assumption concerning the chain-cyclic molecular structure based on the presence of intermolecular and intramolecular hydrogen bonds. Presented by Acad A. N. Terenin 24 Oct 52.

240T8

SHIGORIN, D. N.

Chemical Abstracts
May 25, 1954
Electronic Phenomena
and Spectra

Investigation of the structure of intercomplex compounds by the method of vibration spectra in connection with the question about the nature of the hydrogen bond. D. N. Shigorin. *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.* 17, 596–603(1953).—Raman and infrared spectra of acetylacetonates of Mg, Al, Cr, Fe, Cu, Ni, Zn, Ti, Zr; Cu complexes of derivs. of acetylacetone and acetoacetic ester and Raman spectra of Ni acetylacetonate (in $CHCl_3$) and Zn, Mg, Al acetylacetonates (in dioxane) were investigated. In infrared spectra 2 strong bands appear 1600–1635 cm.$^{-1}$ and 1540–1590 cm.$^{-1}$, whereas in Raman spectra of Al, Mg, Zn, and Ni acetylacetonates weak bands 1507–1520 cm.$^{-1}$ and 1583–1600 cm.$^{-1}$ are detected. The strong bands are attributed to a :C . . . O bond and weak lines to an intermol. metallic bond (in 2 forms—formulas are given). It is shown that the nature of this bond is detd. by the π-electron interaction in the system. The intermol. metallic bond resembles the intermol. H bond in complex mols. It is impossible to explain mol. facts by the donor-acceptor theory of the H bond. The H bond is formed as a result of 3 types of interaction: π-electron, electrostatic (dipole), and action of "undivided" electron pairs. Other causes, including absorption spectra and fluorescence, are cited for the π-electron nature of the H bond in intermol. compds.

S. Paksver

1/14/54

SHIGORIN, D. N.

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Electronic Phenomena dn and Spectra

The Raman spectra of some terpene hydrocarbons. I. T. Dadyshev, P. P. Shorygin, and D. N. Shigorin. *J. Gen. Chem. U.S.S.R.* 22, 631-3(1953)(Engl. translation).—See *C.A.* 46, 7433f. H. L. H.

Shigorin, D N

Study of the structure of keto-enol isomers by the method of vibration spectra. D. N. Shigorin (L. Ya. Karpov Phys. Chem. Inst., Moscow) *Zhur. Fiz. Khim.* 27, 689–702 (1953); cf. *C.A.* 48, 2478*i*.—In order to det. the presence of an enol in $AcCH_2CO_2Et$ (I), Raman spectrograms were made of I alone, and in various solvents. The amt. of enol was detd. from the intensity of the C:C line. Liquid I at 40–45°, freshly prepd. I, and I vapor contained 7, 25, and 50% enol, resp. I mixed with MeOH 10, EtOH 10, C_6H_6 10, Et_2O 10, CCl_4 10, CS_2 13, hexane 88, hexane 27, and hexane 10 mole-% contained 0.7, 12, 16, 27, 25, 20, 9.3, 23, and 50% enol, resp. It was concluded that an enol was present.

J. W. Loweberg, Jr.

SHIGORIN D. N.

USSR/Chemistry - Structural Theory Nov 53

"Some Problems of the Chemical Structure of Molecules. IV," D. N. Shigorin

Zhur Fiz Khim, Vol 27, No 11, pp 1731-1736

Acc to A. M. Butlerov's fundamental law, the chem properties of a mol depend on the arrangement of atoms in it. This law can be extended to the distribution of electrons: there are no typical bonds or typical bond electrons whose nature is independent of the kind of atoms and their specific arrangement. The results of modern quantum chemistry are based on this law, but attempts have been made

274T25

to treat electron distribution without regard to chem structure (e. g. resonance theory). These attempts have failed. Carbon is not always quadrivalent; identification of a chem bond with a pair of electrons is oversimplified and too formalistic. Example of the application of the author's theories to aromatic compds and compds with conjugated bonds are given.

SHIGORIN, D.N.

USSR/ Physics

Card 1/1 Pub. 43 - 48/62

Authors : Shigorin, D. N.

Title : The nature of the H-bond and its effect on energy distribution in oscillation and electron spectra of molecules

Periodical : Izv. AN SSSR. Ser. fiz. 18/6, 723-725, Nov-Dec 1954

Abstract : The infrared absorption spectra of amino-and hydroxy derivatives of anthraquinone as well as hydroxy and amino-azo-compounds were investigated to determine the nature of the H-bond and its effect on energy distribution in the spectra of molecules. The nature of such an H-bond was determined by the fact that the electron of the H-atom participates directly in the reaction with the π - electron of the neighboring atom, and it participates in the transfer of the reaction over the system of conjugated bonds thus promoting accumulation of electrons in the molecule. Four USSR references (1949-1954). Graph.

Institution: The L. Ya. Karpov Phys. Chem. Inst.

Submitted : .....

USSR/Chemistry - Spectral Analysis

Card 1/1

Authors : Shigorii, D. N.

Title : Study of the Structure of Keto-Enol Tautomeric Substances by Means of Oscillation Spectra and Marked Atoms.

Periodical : Zhur. Fiz. Khim. Vol. 28, Ed. 4, 584-593, Apr 1954

Abstract : The study of the structure of keto-enol tautomeric substances, reveals the coexistance in these substances of dienol and monoenol forms, and that the change in structure of enol isomers depends upon the distribution of deutrons in molecules - and vice versa. The experiment shows that the introduction of deutron into some of these systems creates a significant increase of dienol forms. Ten references; tables; graphs; illustrations.

Institution : L. Ya. Karpov's Physico-Chemical Institute, Moscow.

Submitted : June 7, 1952

USSR/ Chemistry - Analytical chemistry

Card 1/1 : Pub. 147 - 13/27

Authors : Bagratishvili, G. D.; Shigorin, D. I.; and Spasokokotskiy, N. S.

Title : The hydrogen bond in indoaniline dyes studied by the infrared absorption spectra method

Periodical : Zhur. fiz. khim. 28/12, 2185-2188, Dec 1954

Abstract : The hydrogen bond and type of bond in indoaniline dyes were investigated by the infrared absorption spectra method. The formation of an intramolecular hydrogen bond between the N - H, O - H and C O groups was established on the basis of absorption spectra obtained. The presence of the intramolecular hydrogen bond in the molecules of the investigated indoaniline dyes was found to cause a sharp displacement of the long wave maximum in the electron absorption spectrum toward long waves. The intensity and wash-out of the spectral bands were evaluated only qualitatively. Twelve references ; 7 USSR; 4 USA and 1 French (1936-1953). Table.

Institution : The L. Ya. Karpov Physico-Chemical Institute and the All-Union Scientific Motion Picture-Photo Institute

Submitted : April 15, 1954

SHIGORIN, D.N.

Investigation of the physical stru[illegible] of synthetic polyam[illegible] by infra-red spectral absorption. D. N. Sh[illegible] N. V. Mik[illegible] and S. P. Makar'eva (Dokl. Akad. [illegible]). Absorption max. are observed at ~3060, 32[illegible] 300 cm.$^{-1}$ in films of cryst. and amorphous polycaprolactam, of which the last is ascribed to intermolecular *trans*-NH...CO bonds, and the other two to intermolecular *cis*- and intramolecular -NH...CO bonds. The 3060 cm.$^{-1}$ peak is sometimes split in crystalline films into two at 3067 and 3090 cm.$^{-1}$, indicatin co-existence of different molecular structures in the films. R. C. MURRAY.

D. N.

USSR.

Investigation of the nature of the mutual effects of atoms and groups by the method of vibration spectra. D. N. Shigorin and N. I. Sheverdina. *Doklady Akad. Nauk S.S.S.R.* 96, 561–4 (1954).—Vibration spectra of the following F-contg. compds. were studied: Et trifluoroacetate, trifluoroacetone, Et trifluoroacetoacetate, and hexafluoroacetylacetone.

Gladys S. Macy

SHIGORIN, D. N.

USSR/Chemistry

Card : 1/1

Authors : Shigorin, D. N.

Title : Mutual effect of atoms and groups investigated by the oscillating spectra method

Periodical : Dokl. AN SSSR, 96, Ed. 4, 769 - 772, June 1954

Abstract : The intensity of a band, in infrared absorption spetra, connected with the magnitude of the dipole monent of the group, its change during oscillations and dependence upon the nature of the electron excitation of the molecule, are explained. During the formation of a molecule, as result of the mutual effect of atoms, a change occurs in the valent states, in the energy levels of the electron, and nature of their motion. A small increase in the band intensity in the infrared spectrum indicates a small increase in the dipole moment of the group. Seven references. Table.

Institution : The L. Ya. Karpov Physico-Chemical Institute

Presented by: Academician V. M. Rodionov, February 1, 1954

SHIGORIN, D. N.

USSR/ Chemistry - Physical chemistry

Card 1/1 : Pub. 22 - 36/46

Authors : Shigorin, D. N; Mikhaylov, N. V.; and Makaryeva, S. P.

Title : The physical structure of synthetic polyamides investigated by the infrared absorption spectra method

Periodical : Dok. AN SSSR 97/4, 711-714, Aug 1, 1954

Abstract : The application of the infrared absorption spectra method for the physico-chemical study of synthetic polyamides, is discussed. A comparison of absorption spectra of various synthetic polyamides showed that the structure of the latter is determined by a combination of three (alpha, beta, gamma) H-bonds. The existence of the three basic H-bonds in synthetic polyamides, which in fact determine their physical structure and chemical properties, was positively established. These three H-bonds are also responsible for the crystalline lattice of the synthetic polyamides. Eight references: 4-USSR and 4-USA (1936-1954). Table; drawing.

Institution : All-Union Scientific-Research Institute of Synthetic Fibers

Presented by : Academician V. A. Kargin, May 10, 1954

Shigorin, D.N

K-6

USSR/Optics - Spectroscopy

Abs Jour : Referat Zhur - Fizika, No 5, 1957, 13010

Author : Shigorin, D.N., Dokunikhin, N.S., Gribova, Ye.A.

Inst :

Title : Vibrational and Electronic Spectra of Indigo and its Halide Derivatives.

Orig Pub : Zh. fiz. khimii, 1955, 29, No 5, 867-876

Abstract : An investigation was made of the absorption spectrum of indigo (I). thioindigo (II), tetrachloro-indigo (III), and tetrabromo-indigo (IV) in the visible and infrared regions. In the apectrum of a crystal of I, the frequency of the valent N-H vibrations is reduced to 3275 cm^{-1}, owing to the formation of intermolecular hydrogen bonds M -- H...O = C. In the spectrum of vapors of I, the frequency of the N -- H vibrations comprises 3405 cm^{-1}, and the electron absorption shifts by 100 millimicrons towards the short-wave side, owing to changes in the

Card 1/2

USSR/Optics - Spectroscopy

Abs Jour : Ref Zhur - Fizika, No 5, 1957, 13010

K-6

distribution of the π-electron density during the break of the hydrogen bonds. There are no intermolecular hydrogen bonds in crystals of III and IV, since the frequency of the C = O oscillations, 1650 cm^{-1}, does not differ from the C = O frequency in II. It is assumed that there exists weak intra-molecular hydrogen bonds N-H...X (X is iether Cl or Br); the N -- H band os less shifted than in I (3385 cm^{-1}), and is less intense. In III and IV no considerable changes in the electronic spectra are observed upon transition from the crystal to the solution, in accordance with the assumption concerning the intra-molecular hydrogen bonds. An attempt is made of explaining qualitatively the changes in the coloring of the derivatives of I as functions of the influence of various substitutes or of the intermolecular interaction on the distribution of the π-electron density.

Card 2/2

SHIGORIN, D.N.

Investigation of the chemical structure of isatin and its salts by means of infra-red absorption spectra. Zhur.fiz.khim. 29 no.6:1033-1041 Je '55. (MLRA 9:1)

1.Fiziko-khimicheskiy institut imeni L Ya.Karpova, Moscow.
(Isatin--Spectra)

SHIGORIN, D.N.

USSR/ Chemistry - Physical chemistry

Card 1/1 Pub. 147 - 4/22

Authors : Shigorin, D. N., and Dokunikhin, N. S.

Title : Nature of the hydrogen bond and its effect on the oscillation and electron spectra of molecules

Periodical : Zhur. fiz. khim. 29/11, 1958-1973, Nov 1955

Abstract : The infrared absorption spectra of numerous compounds of oxy-and amino derivatives of anthraquinone were measured in the valent oscillation zone of C = O, O - H and N - H groups. It was found that the intramolecular hydrogen bond included in the conjugated bond system causes considerable changes in the π -electron reaction in the entire molecule and a certain change in energy of the system on the whole. The stability of such hydrogen bonds is discussed. It was established that a hydrogen bond with a π -electron interaction is a weak link in the chain of π -electron excitation. Twenty references: 15 USSR, 3 USA and 2 Germ. (1914-1955). Tables; graph.

Institution : The Physicochemical Institute im. L. Ya. Karpov, Moscow

Submitted : May 19, 1955

SHIGORIN, D. N.

USSR/ Physics - Physical chemistry

Card 1/2 Pub. 22 - 33/52

Authors : Shigorin, D. N., and Dokunikhin, N. S.

Title : The nature of the hydrogen bond and its effect on energy distribution in oscillatory and electron spectra of molecules

Periodical : Dok. AN SSSR 100/2, 323-326, Jan 11, 1955

Abstract : Two cases of formation of hydrogen bonds of uniform nature are cited. The problem concerning the nature of hydrogen bonds and its manifestation in electron spectra of molecules is discussed. The formation of a single electron cloud which binds two oxygen and proton atoms was observed in the presence of relatively small spaced between the atoms in the O - H - O bond.

Institution : The L. Ya. Karpov Scient.-Research Physico-Chemical Institute

Presented by : Academician A. N. Terenin, April 20, 1954

Periodical : Dok. AN SSSR 100/2, 323-326, Jan 11, 1955

Card 2/2 Pub. 22 - 33/52

Abstract : The inclusion of the hydrogen atom in the π-electron reaction of the molecule is followed by a specific deformation of the electron cloud and corresponding energy changes. Deformation of the electron cloud of the H atom during the formation of an intramolecular bond with the π- electron effect was found to be different from the deformation where the dipole effect plays an important role in the H-bond formation. Eight references: 5 USSR, 2 USA and 1 German (1914-1953). Diagram

SHIGORIN, D.N.

USSR/Chemistry - Physical chemistry

Card 1/2 Pub. 22 - 36/60

Authors : Shigorin, D. N., and Dokunikhin, N. S.

Title : Appearance of a hydrogen bond in oscillatory and electron spectra of amino substitutes of anthraquinone

Periodical : Dok. AN SSSR 100/4, 745-748, Feb 1, 1955

Abstract : The absorption spectra in the infrared zone were investigated for a large group of amino substitutes of anthraquinone to determine the relations between the spatial orientation of the groups which take active part in the formation of hydrogen bonds and the nature of their appearance in oscillatory and electron spectra of molecules. It was observed that the conversion of the solid dye into vaporous state as result of the disturbance of the inter- and intramolecular hydrogen bonds is followed by a sudden change in its oscillatory and electron spectra. It was determined that the intramolecular hydrogen bond is capable of causing certain changes in

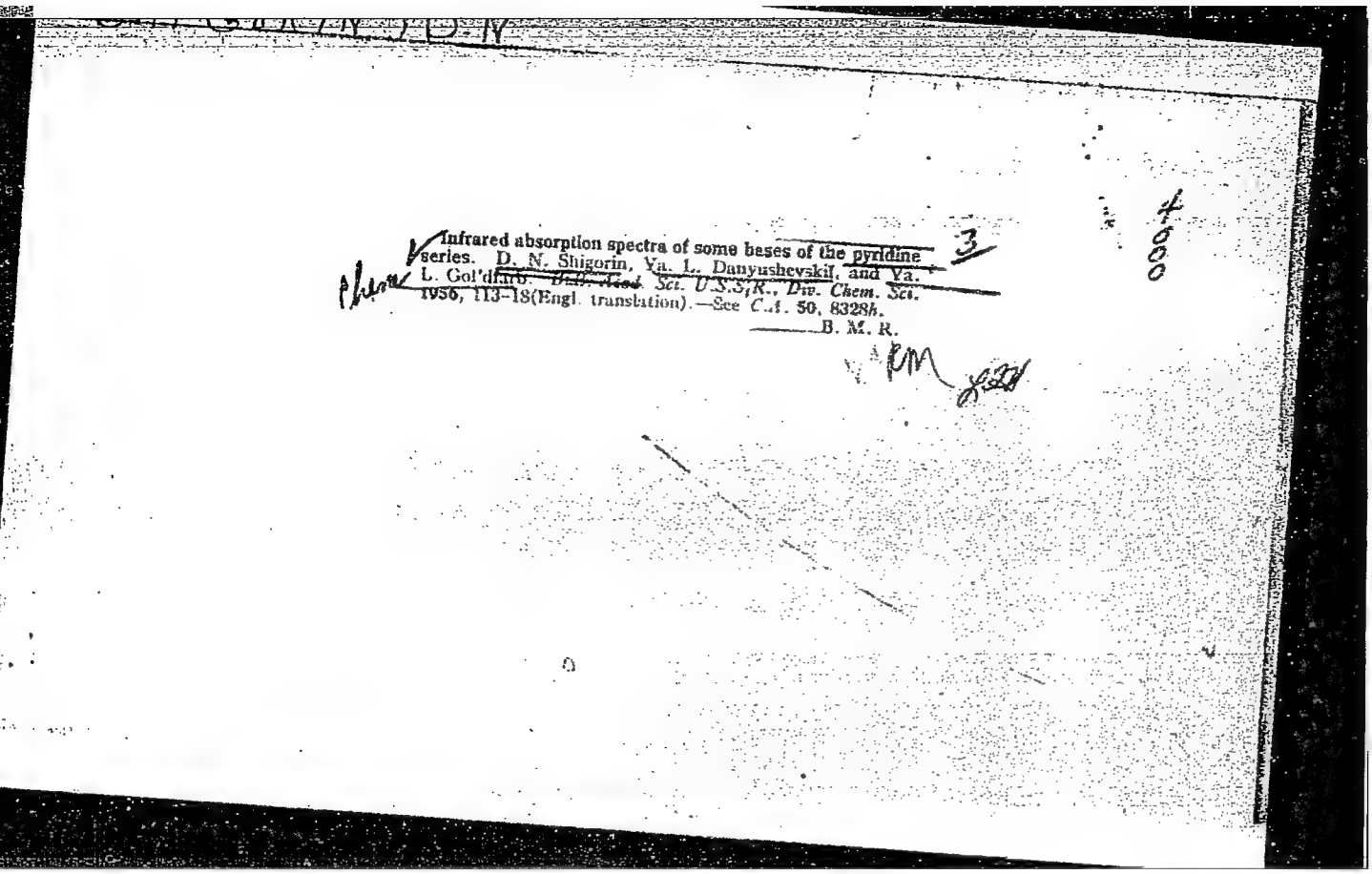
Institution : The L. Ya. Karpov Scientific Research Phys-Chem. Institute

Presented by: Academician A. N. Terenin, June 21, 1954

Periodical : Dok. AN SSSR .00/4. 745-748, Feb 1, 1955

Card 2/2 : Pub. 22 - 36/60

Abstract : the distribution of the π-electron density in the molecule even if the electron of the hydrogen atom does not directly react with the π-electron of the neighboring group. Five USSR references (1949-1954). Diagram.



Infrared absorption spectra of some bases of the pyridine series. D. N. Shigorin, Va. L. Danyushevskiĭ, and Va. L. Gol'dfarb. *Doklady Akad. Sci. U.S.S.R., Div. Chem. Sci.* 1956, 113–18(Engl. translation).—See *C.A.* 50, 8328*h*.

B. M. R.

USSR/ Chemistry - Organic chemistry

Card 1/1 Pub. 40 - 21/25

Authors : Shigorin, D. N.; Danyushevskiy, Ya. L.; and Gol'dfarb, Ya. L.

Title : Infrared absorption spectra of certain bases of the pyridine series

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 120-126, Jan 1956

Abstract : A comparison of the infrared absorption spectra of alpha-aminopyridine and alpha-pyridoneimine compounds showed that the multiple bond nitrogen atom is the most basic one in these compounds. The nitrogen atom in this case functions as the salt-forming center. It was established that the addition of N to the side chain atom in alpha-pyridoneimine derivatives lead to over-distribution of the electron density followed by the origination of a "benzoid" structure of the molecule. The distribution of the positive charge between the nitrogen atoms is explained. Eight USSR and USA references (1938-1953). Tables.

Institution : Acad. of Sc., USSR Inst. of Organ. Chem. im. N. D. Zelinskiy and the Physico-Chemical Inst. im. L. Ya. Karpov

Submitted : February 15, 1955

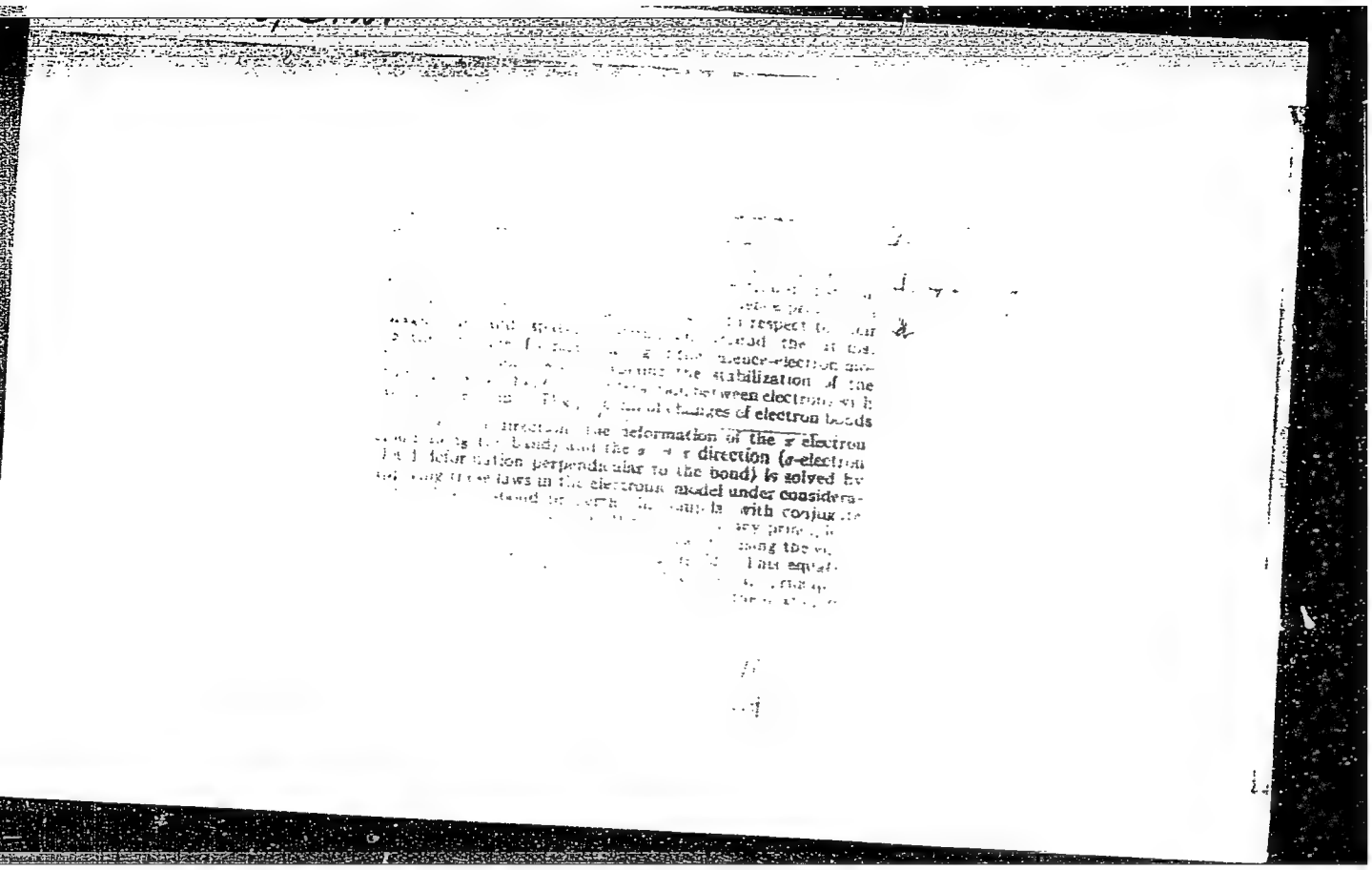
GOL'DFARB, Ya.L; KONDAKOVA, M.S.; SHIGORIN, D.N.

Study of the hydrogen bond in α-aminonicotine by comparison of the infrared absorption spectra. Izv.AN SSSR.Otd.khim.nauk no.3: 336-339 Mr '56. (MLRA 9:8)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii nauk SSSR i Fiziko-khimicheskiy institut imeni L.Ya. Karpova.
(Pyridine--Spectra)

V Investigation of the structure of the polypeptide bond by means of infrared absorption spectra. [illegible] D. N. Shigorin. [illegible] Chem. Inst. [illegible] Ya. Karpov [illegible] Phys. Khim. 30, 1551-5 [illegible] synthetic polyamides, α-keratin, wool, fibroin, and natural silk, bands were established corresponding to the valence bonds of the peptide groups, participating in H bonds in stretched (β) and relaxed (α) polypeptide chains. The 3210-cm.$^{-1}$ absorption corresponds to the N—H··· in the folded chain, internally H bonded. The 3330- and 3080-cm.$^{-1}$ absorptions correspond to the N—H··· in the extended chain, H bonded, resp., trans and cis to a CO on an adjacent chain. In stretched fibers only these last frequencies appear, but in relaxed ones the former frequencies appear as well. Conclusions drawn from infrared data agree well with those from x-ray data.

J. P. Danehy



Shigorin, D.N.

USSR/ Physical Chemistry - Molecule. Chemical Bond. B-4

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7233

Author : Shigorin, D.N., Shemyakin, M.M., Shchukina, L.A., Kolosov, M.N., and Mendelyevich, F.A.

Inst : Academy of Sciences USSR

Title : On the Nature of the Intramolecular Hydrogen Bond

Orig Pub : Dokl. AN SSSR, 1956, Vol 108, No 4, 672-675

Abstract : The IR spectra of molecules with intramolecular hydrogen bonds (HB) involving different degrees of participation of the π-electrons of the C=O group and of the multiple bonds conjugated with it have been investigated. The frequency of the valency vibrations of the O-H groups (the first number in parentheses, in cm^{-1}) and their shift towards longer wavelengths in comparison to the unassociated OH groups (second number in parentheses) as well as the BH energy (Badger and Bauer, J. Chem. Phys., 1937, 5, 839) (third number in parentheses in kcal), the

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USSR/ Physical Chemistry - Molecule. Chemical Bond. B-4

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7233

fractional contribution of π-electron interaction energy to the total BH energy in percent (fourth number in parentheses), and the interatomic O...H distance calculated from standard bond dist. and the bond angles (fifth number in parentheses in A.U.) have been determined for the following compounds: the vapor of the nonomethyl ether of ethylene glycol (I) at 120-122°(3665, 0, 0, 0, -); I in CCl_4 (II), in the ratio 1:400 (3605, 60, 0.96, 0, 1.80); phenol in II, 1:400 ratio (3605, 0, 0, 0, -); guaiacol in II, 1:400 (3530, 55, 0.90, 0, 2.20); oxyoctenol in II, 1:400 (3475, 147, 2.38, 59.7, 1.95); benzoin in II, 1:400 (3468, 147, 2.39, 60.0, 1.95); 2-hydroxy-1, 4-naphthoquinone in II, 1:400, 3398 (187, 3.07, 68.7, 2.25); 2-benzyl-3-hydroxy-1, 4-naphthoquinone in II, 1:600 (3395, 190, 3.11, 69.1, 2.25); 2-(β-naphthyl)-3-hydroxy-1, 4-naphthoquinone in II, 1:600 (3370, 215, 3.52, 72.7, 2.25); β-methyltropinone in II, 1:400 (3116, 504, 8.19, 88.2,

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2.25); vapor of the monomethyl ether of trimethylene glycol (III) at 160° (3650, 0, 0, 0, -); III in II, 1:400 (3580, 70, 1.12, 0, 1.65); o-methoxybenzyl alcohol (IV) vapor at 163-164° (3652, 0, 0, 0, -); IV in II 1:400 (3585, 67, 1.08, 0, 1.65); diacetone alcohol in II, 1:400 (3524, 94, 1.52, 26.2, 1.65); methyoxybenzoic acid in II, 1:400 (3357, 228, 3.74, 70.0, 1.65); salicylic acid vapor at 144° (3265, 320, 5.25, 78.7, 1.65); salol in II, 1:400 (3230, 355, 5.82, 80.7, 1.65); methyl salicylate in II, 1:400 (3205, 380, 6.23, 82.0, 1.65); acetylacetone in II, 1:400 (3050, 570, 9.26, 87.9, 1.65); monomethyl ether of 1, 8-dihydroxynaphthalene in II, 1:400 (3431, 189, 3.07, 63.5, 1.63); 9-hydroxy-1-methoxy-7-oxy-9-methyl-5,6,7,8-tetrahydroanthracene in II, 1:600 (3620, 0, 0, 0, -); 10-hydroxy-1-methoxy-7-oxy-9-methyl-5,6,7,8-tetrahydroanthracine in II, 1:400 (3423, 197, 3.20, 65.0, 1.63); 10-hydroxy-1-methoxy-9-methyl-

B-4

USSR/ Physical Chemistry - Molecule. Chemical Bond.

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7233

5,6,7,8-tetrahydroanthracene in II, 1:400 (3425, 195, 3. 16, 64.5, 1.63); alizarin vapor at 290° (3150 (x), 470, 7.64, 85.3, 1.65); 1, 8-dihydroxyanthraquinone vapor at 300° (3150, 470, 7.64, 85.3, 1.65); On the basis of the data obtained, the authors conclude that the magnitude of the π -electron interaction energy depends on: (1) The presence of a system of conjugated bonds comprising both the HB group and the rest of the molecule; (2) An even number of terms in that system; (3) The planarity of the HB groups and the other parts of the molecule; and (4) The number and nature of the distribution of π -electrons in the system.

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SHIGORIN, D.M.,

"The Nature of the Hydrogen Bond and its Influence on the Vibrational and Electronic Spectra of Molecules," report submitted at IUPAP Symposium on Nature of Hydrogen Bonding, Ljubljana, Yugoslovakis, 30 July - 3 Aug 57.

Trans. Encl. B-3,096,177, 20 Jan 58

SHIGORIN, D.N.

PRIKHOT'KO, A.F.

24(7) p.3 PHASE I BOOK EXPLOITATION SOV/1365

L'vov. Universytet

Materialy I Vsesoyuznogo soveshchaniya po spektroskopii. t. 1: Molekulyarnaya spektroskopiya (Papers of the 10th All-Union Conference on Spectroscopy. Vol. 1: Molecular Spectroscopy) [L'vov] Izd-vo L'vovskogo univ-ta, 1957. 499 p. 4,000 copies printed. (Series: Its: Pizychnyy zbirnyk, vyp. 3/8/)

Additional Sponsoring Agency: Akademiya nauk SSSR. Komissiya po spektroskopii. Ed.: Lazer, S.L.; Tech. Ed.: Saranyuk, T.V.; Editorial Board: Landsberg, G.S., Academician (Resp. Ed., Deceased), Naporent, B.S., Doctor of Physical and Mathematical Sciences, Fabelinskiy, I.L., Doctor of Physical and Mathematical Sciences, Fabrikant, V.A., Doctor of Physical and Mathematical Sciences, Kornitskiy, V.G., Candidate of Technical Sciences, Rayskiy, S.M., Candidate of Physical and Mathematical Sciences, Klimovskiy, L.K., Candidate of Physical and Mathematical Sciences, Miliyanchuk, V.S., Candidate of Physical and Mathematical Sciences, and Glauberman, A. Ye., Candidate of Physical and Mathematical Sciences.

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Nazarov, I.N., L.A. Kazitsyna, and I.I. Zaretskaya. Determination of the Structure of Carbonyl Compounds From Absorption Spectra of Their 2,4-dinitrophenylhydrazones 185

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Card 13/30

SHIGORIN, D.N

AUTHOR: Vol'kenshteyn, M. V., Doctor of Physico-Mathematical Sciences

TITLE: An International Symposium on the Hydrogen Bond in Ljubljana (Mezhdunarodnyy simpozium po vodorodnoy svyazi v Lyublyane)

PERIODICAL: Vestnik AN SSSR, 1957, Vol. 27. Nr 11, pp. 137-139 (USSR)

ABSTRACT: Scientists from Yugoslavia, the West- and Easteuropean countries, Australia, the USA, Canada, the USSR, Scandinavia and the state of Israel participated in the symposium held from July 29 to August 3. More than 60 speakers got a hearing. The soviet delegation read 6 papers: Ye.F.Gross talked on "The vibration spectrum of the hydrogen bond". D.N.Shigorin on "The nature of the hydrogen bond and its influence upon the vibration- and electron-spectra of the molecules", V.M.Chulanovskiy on "The spectroscopic investigation of the hydrogen bond", M.V.Vol'kenshteyn on "The behavior of the hydrogen bonds in vitrification (steklovaniye)", N.D.Sokolov "On the quantum theory of the hydrogen bond", A.N.Terenin and V.Filimonov "The hydrogen bond between adsorbed molecules and the structural OH-groups on the surface of solid bodies". Many papers were devoted to the spectroscopy of the hydrogen bond. Important information was

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given by Dzh.Pimentel (USA) on the spectral properties of the compounds at low temperatures and G.Marrinan (England) on the investigation-results of the crystalline modifications of cellulose by means of the method of polarized infrared spectra. E. Lippert (German Federal Republic) gave an extensive survey of the influence exerted by the hydrogen bonds upon the electron-spectra. The session in which the participants especially dealt with the problems of the crystallography of the compounds with those of hydrogen, was opened by Dzh.Bernal, England, with an extensive report on the part played by the hydrogen bonds in solids and in liquids for which the participants showed great interest. R.Pepinskiy (USA) talked on the investigation of the hydrogen bond by means of the X-ray and neutronographic method. U.Shneyder (Canada) and others also dealt with this method. The following sessions mainly dealt with problems of the theory of the hydrogen bond. Speaker was: Ch.Koulson, England. His statement caused a lively discussion in which above all the American scientists participated. Although there exists no strict definition on the conception of the hydrogen bond, all participants in the discussion agreed that the evidence of the quantum-mechanical process of the formation of a donor-acceptor bond (donorno-aktseptornaya svyaz') were necessary for the

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SHIGORIN, D. N.

"Typical bands in infrared adsorption spectra" with N. V. Mikhaylov

Report presented at the 10th All-Union Conf. on Highly Molecular Compounds, Moscow, 11-15 June 1950. (Vest. Ak Nauk SSSR, 1950, No. 9, pp. 111-113)

SOV/58-59-8-17578

Translated from: Referativnyy Zhurnal Fizika, 1959, Nr 8, p 89 (USSR)

AUTHOR: Shigorin, D.N.

TITLE: The Nature of Hydrogen and Metallic-Element Bonds and Their Influence on the Vibration and Electronic Spectra of Molecules

PERIODICAL: In the symposium: Probl. fiz. khimii. Nr 1. Moscow, Goskhimizdat, 1958, pp 173 - 201

ABSTRACT: The survey considers the cases of hydrogen bonds without π-electrons and with π-electrons, metallic-element intramolecular bonds in molecules with π-electrons and the case of intermolecular metallic-element bonds. The hydrogen bond without π-electrons is determined by the energy of the acceptor-donor and dipole interaction. An explanation is given of the experimental data concerning the significantly greater smearing and stronger shifting towards the lower frequencies and of the higher by many times integral intensity of the bands of the valence vibrations of the ...O-H... groups of polymer chains, as compared with the bands of the O-H... group. In the general case the hydrogen bond develops on account of the dipole, acceptor-donor (with the participa-

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SOV/58-59-8-17578

The Nature of Hydrogen and Metallic-Element Bonds and Their Influence on the Vibration and Electronic Spectra of Molecules

tion of the "undivided" electron pair) and π-electronic interaction. The article discusses the relation between the degree of participation of π-electrons in the realization of an intramolecular hydrogen bond and the structure of the molecule. The intramolecular metallic-element bond in molecules with π-electrons is examined in an analogous manner. In intracomplex compounds the indicated bonds connect the individual parts of the molecule by means of π-electronic interaction, and render the system energetically stable and united. The hydrogen bond is considered to be a particular case of the secondary (weak) chemical bond. Primary (strong) chemical bonds develop on account of the direct interaction of the valence electrons of the atoms. The article gives a bibliography containing 31 titles.

V.V. Shmidt

Card 2/2

SHIGORIN, D.

62-1-28/29

AUTHORS: Rodionov, A., Shigorin, D., Talalayeva, T., Kocheshkov, K.

TITLE: Letters to the Editor (Pis'ma redaktoru)

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 1, pp. 120-120 (USSR)

ABSTRACT: On the strength of the research of the infrared spectra of the compounds R - Li and R - O - Li the authors of this letter discovered the formation of an intermolecular lithium binding $-\delta\ +\delta\quad -\delta\ +\delta$ C—Li....C—Li.... and $-\delta\ +\delta\quad -\delta\ +\delta$ O—Li....O Li... A comparison of the spectra of the vapors, solvents, and powders in vaseline oil as well as an analysis of the kind of oscillation of the molecules made possible the precise determination of the frequency of the valent oscillations of the groups C--Li (of the free and those taking part in the formation of the lithium binding; see table). The intermolecular lithiumbinding $-\delta\ +\delta$ -C...Li- is constant. With the binding $+\delta\ -\delta$ -Li...O- the latter is, however, still more stable. The formation of especially resistent intermolecular lithium bindings has to be traced back to the peculiarity of the atom of the lithium: Small

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Letters to the Editor

radius, comparatively small ionization potential, better possibility of utilizing the -orbit. All this makes possible a immediate more and more active taking part of its electron in the intermolecular interaction than is the case with the hydrogen atom. There is 1 table.

ASSOCIATION: Physicochemical Institute imeni L. Ya. Karpov (Fiziko-Khimicheskiy institut imeni L. Ya. Karpova).

SUBMITTED: December 20, 1957

AVAILABLE: Library of Congress

1. Lithium-Molecular structure 2. Vaseline oil spectra-Analysis
3. Infrared spectra-Applications

Card 2/2

Conference on Molecular Spectroscopy in London SOV/30-53-6-15/45

the works of the Soviet scientists A.N.Terenin, N.G.Yaroslavskiy and A.N.Sidorov in this field, reported on the investigation of infrared spectra of adsorbed molecules. M.M.Sushchinskiy described the method of analysis of the molecular structure of hydrocarbons by means of their spectra of dispersion. After the end of the conference, the Soviet delegation had a chance to become acquainted with work carried out in the field of molecular spectroscopy in a series of English laboratories.

1. Molecular spectroscopy--USSR

Card 2/2

51-4-2-25/28

AUTHORS: Shigorin, D. N. and Bagratishvili, G. D.

TITLE: Infrared Spectra and Chemical Structure of Aminoazodye Hydrochlorides. (Infrakrasnyye spektry i khimicheskoye stroyeniye gidrokhloridov aminoazokrasiteley.)

PERIODICAL: Optika i Spektroskopiya, 1958, Vol.IV, Nr.2, pp.274-278 (USSR)

ABSTRACT: It is reported (Refs.1-3) that aminoazohydrochlorides exist in two tautomeric forms: with azido and quinohydrazone structure. The present authors (Refs.4-5) deduced from the infrared absorption spectra that oxy- and aminoazo-compounds of benzene and naphthalene series possess only azido structure. In the present paper the authors study the chemical structure of hydrochlorides of aminoazo-compounds and the effect of an internal molecular hydrogen bond in o-isomers on formation of salts. The authors studied the infrared absorption spectra in the 2.5-5 μ region of hydrochlorides of n-aminoazobenzene (II in the table on p.275), 1-benzoazo-4-naphthylamine (III) and 1-benzoazo-2-naphthylamine (IV). Spectra of α-naphthylamine hydrochloride are also given in that table (I). The infrared absorption spectra were measured using an IKS-1 spectrometer with a lithium fluoride prism. The

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51-4-2-25/28

Infrared Spectra and Chemical Structure of Aminoazodye Hydrochlorides.

spectra were obtained on crystals in paste form. They are shown in the figure on p.276. From the infrared spectra obtained by them the authors conclude that in hydrochlorides of n-aminoazo-compounds the proton is joined to the nitrogen of the azo-group. The studied hydrochlorides of n-aminoazo-compounds were found to have only azido structure. As in aminoazo-compounds themselves (Ref.5) the infrared spectra of hydrochlorides of compounds of the o-series differ strongly from the spectra of hydrochlorides of the n-series (see table and figure), both in the position and intensity of bands. This difference in spectra is explained as follows. Although in both the n-isomer and o-isomer hydrochlorides the proton is attached to the nitrogen (of the azo-group and amino-group, respectively), in the o-compounds this attachment is accompanied by disturbance of the internal hydrogen bond. There are 1 figure, 1 table and 10 references of which 6 are Soviet, 2 German, 1 French and 1 English.

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51-4 -2-25/28

Infrared Spectra and Chemical Structure of Aminoazodye Hydrochlorides.

ASSOCIATION: Physico-Chemical Institute imeni L.Ya. Karpov.
(Fiziko-khimicheskiy institut im. L.Ya. Karpova.)

SUBMITTED: May 29, 1957.

1. Aminoazodye hydrochlorides-Infrared spectra 2. Aminoazodye hydrochlorides-Structural analysis

Card 3/3

SOV/62-58-9-22/26

AUTHORS: Shigorin, D. N., Shemyakin, M. M., Kolosov, M. N.

TITLE: Intermolecular Interactions Between Acetylene and Its Derivatives (Mezhmolekulyarnyye vzaimodeystviya u atsetilena i yego proizvodnykh)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 9, pp 1133 - 1134 (USSR)

ABSTRACT: Considering the peculiarities of the chemical structure of acetylene and its derivatives the authors considered it possible that these compounds might be able to form complexes with one another and with solvents. These complexes could result from the hydrogen bridge bonds R-C ≡ C-H.X (X= O<, O = C<, N<, —C ≡ C, and so forth). The study of the infrared absorption spectra showed frequency changes in the ≡ C-H and — C≡C - groups of acetylene and its derivatives in dissolving in acetone, ether, pyridine, and dioxane, in sublimating from the crystalline to the vapor state and in solutions of CCl_4. This probably means that the acetylene molecule forms complexes with the molecules

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Intermolecular Interactions Between Acetylene and Its Derivatives SOV/62-58-9-22/26

of the solvent by forming hydrogen bonds. The union of the acetylene molecules and the homologs and derivatives of acetylene is apparently possible because of the electron shift in the ≡C - H and -C≡C- bonds (which also belong to many other molecules). For this reason intermolecular electron orbitals are hypothesized. The authors discovered a new phenomenon in intermolecular interaction. It was shown experimentally that the formation of hydrogen bridge bonds and π complexes among the molecules of acetylene and its derivatives is possible. It was demonstrated that the hydrogen of the ≡ C-H group exchanges with deuterium in the dissolution of R - C≡CH compounds in CH_3OD or C_2H_5OD. For R-C≡CD in CCl_4 the following frequencies were found:

$\nu(\equiv C\text{-}D) = 2600\ cm^{-1}$; $\nu(-C\equiv C-) = 1957\ cm^{-1}$. There is 1 table.

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Intermolecular Between Acetylene and Its SOV/62-58-9-22/26
Derivatives

ASSOCIATION: Fiziko-khimicheskiy institut im.L.Ya.Karpova (Physical-Chemical Institute imeni L.Ya.Karpov) Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences of the USSR)

SUBMITTED: June 24, 1958

Card 3/3

SOV/48-22-9-27/40

AUTHORS: Rodionov, A. N., Shigorin, D. N., Talalayeva, T. V., Kocheshkov, K. A.

TITLE: Infrared Absorption Spectra of Organolithium Compounds (Infrakrasnyye spektry pogloshcheniya litiyorganicheskikh soyedineniy) Intermolecular Lithium Binding (Mezhmolekulyarnaya litiyevaya svyaz')

PERIODICAL: Izvestiya Akademii nauk SSSR. Seriya fizicheskaya, 1958, Vol 22, Nr 9, pp 1110 - 1113 (USSR)

ABSTRACT: In this paper a report is given on the discovery and the investigation of the intermolecular lithium binding $-\overset{-\delta}{C} - \overset{+\delta}{Li} \ldots \overset{-\delta}{C} - \overset{+\delta}{Li}$ ... and $-\overset{-\delta}{O} - \overset{+\delta}{Li} \ldots \overset{-\delta}{O} - \overset{+\delta}{Li}$ ... which were based upon the study of the infrared spectra of compounds of the type R - Li and R - O - Li. The intermolecular lithium binding $-\overset{+\delta}{Li} \ldots \overset{-\delta}{C}$ - must be granted special importance because it can be formed without cooperation of the acceptor-donor interaction. The required compounds were synthetized and purified according to the method developed by Kocheshkov et al. (Refs 9,10). The spectra

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were recorded of vapors, solutions and powder in vaseline oil (Figs 1,2). A comparison of the spectra and the analysis of the nature of the oscillation of the molecules permit to determine the frequencies of the valence oscillations of free and of C-Li groups taking part in the formation of the lithium binding (Table 2). The intermolecular lithium binding $-C^{-\delta} \cdots Li^{+\delta}$ - is stable ($\frac{\Delta\nu}{\nu_o}$ = 12 - 19%) notwithstanding the fact that it is produced without cooperation of the acceptor-donor interaction. Even more stable is the binding $Li^{+\delta} \cdots O^{-\delta}$ -. As was mentioned before, the $-Li^{+\delta} \cdots C^{-\delta}$- binding is formed without the cooperation of the acceptor-donor interaction. in this connection the problem of the nature of this bond arises. It is known that the electrostatic interaction is unable to explain completely the formation and the properties of such molecular compounds. The explanation of this phenomenon can probably be sought in the particular

Infrared Absorption Spectra of Organolithium Compounds. SOV/48-22-9-27/40
Intermolecular Lithium Binding

nature of the lithium atoms. It is possible that in the case under review the nature of the lithium bond can principally be explained by the immediate interaction of the electron from the lithium atom, which is in a p-state together with the "free part of the electron density" of the carbon atom and partly also by the dipole interaction. There are 2 figures, 2 tables, and 14 references, 11 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im.L.Ya.Karpova (Institute of Physical Chemistry imeni L.Ya.Karpov)

Card 3/4

76-32-4-26/43

AUTHORS: Konkin, A. A., Shigorin, D. N., Novikova, L. I.

TITLE: The Infrared Absorption Spectra of Monosaccharides and Polysaccharides (Infrakrasnyye spektry pogloshcheniya mono- i polisakharidov)

PERIODICAL: Zhurnal Fizicheskoy Khimii, 1958, Vol. 32, Nr 4, pp. 894 - 903 (USSR)

ABSTRACT: As an introduction the present paper explains the possibilities of the types of hydrogen bindings in mono- and polysaccharides and mentiones two basic types. It is pointed out that the investigations carried out hitherto by means of infrared spectroscopy for the purpose of determining the types of hydrogen binding by observing the position and diffusion of spectral bands of the OH-group of polysaccharides are insufficient. The present experiments deal with the investigations of mono- and polysaccharides as well as of polyatomic alcohols, with comparisons of the spectra being carried out to solve the problem of the function of the absorption spectrum of the hydroxyl

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The Infrared Absorption Spectra of Monosaccharides and Polysaccharides

groups on their geometrical distribution within the molecule. The measurements were carried out by means of a ИКС-11 spectrometer with a Nernst rod as source of radiation; the results obtained are shown on tables and graphically as well. Among other it was observed that in d-glucoses and d-xyloses both types of hydrogen binding are existing (I. -O-H ....O-H...O-H and II. -O-H...O-H). The spectrum of d-galactosis shows two strong low-frequency bands 3120 and 3206 cm^{-1} which points at the presence of a greater number of bindings of type I. In the rest of the monosaccharides, on the other hand, also characteristic phenomena were observed, the explanation of which needs detailed structural investigations. The investigations of polyatomic alcohols showed that, for instance, a difference between mannite and xylite consists of the fact that the latter has more bindings of type I. Based on the spectral analyses of polysaccharides the energies of hydrogen bindings were determined and a closer classification of the relative intensity of intermolecular interactions was carried out. The energy changed

The Infrared Absorption Spectra of Monosaccharides and Polysaccharides

4 - 6 kcal., the highest value having been obtained with cellulose. As final conclusion the change of energy of the intermolecular interaction is given as follows: cellulose > amylosis > xylan > laminarine > galactan. There are 6 figures, 2 tables and 12 references, 5 of which are Soviet.

SUBMITTED: January 8, 1957

AVAILABLE: Library of Congress

1. Monosaccharides--Spectrographic analysis 2. Polysaccharides --Spectrographic analysis 3. Polyatomic alcohols--Spectrographic analysis 4. Infrared spectroscopy--Applications

AUTHOR: Shigorin, D. N. SOV/76-32-8-6/37

TITLE: An Electron Model of the Chemical Structure of Molecules. II (Ob elektronnoy modeli khimicheskogo stroyeniya molekul. II)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol. 32, Nr 8, pp. 1739-1762 (USSR)

ABSTRACT: Continuing an earlier paper (Ref 1) the results mentioned therein are explained. For this purpose a function of the properties of the atoms or bonds versus the characteristic properties of the chemical structure of the molecule had to be found according to the conceptions of A. M. Butlerov. The following factors may be regarded as basic elements of the ordering of chemical bonds determining the properties of the bonds or the atoms: First the number of atoms surrounding the given atom or bond. Second the nature of the atoms characterized by the electronegativities (Z_x, Z_c). Third the geometrical order and the state of valence of the atoms. Therefore the function $S = (n, n_1, n_2, Z_x, Z_c)$ must be found (where n denotes the number of the nearest, n_1 that of the following, and n_2 that of

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An Electron Model of the Chemical Structure of Molecules. II

remote neighboring atoms); for this purpose the corresponding assumptions must be made. These have been explained already in other papers by the same authors. The "unsaturated character" of the atoms and the index of the free valence F, respectively, are investigated and the equation $F = 1 - 0,358n + 0,0593n_1 - 0,005n_2$ is mentioned, according to which data similar to those by Pullman (Pul'man) (Ref 3) were obtained. Values according to L. Poling (Ref 4) were used for the modification of this calculation formula for hetero atoms. Then equations for a random atom of the integrals β are derived, and it is found that atoms of the given type have the same values for F and β. In calculating the interatomic distances the data from the book by D. I. Kitaygorodskiy (Ref 6) are used and the formula $l = 1,54 - 0,048n + 0,008n_1$ is mentioned for the bond length C⋯⋯C in chain molecules; in agreement with the results obtained by G. V. Bykov (Ref 8) is found. The magnitude of the π-electron density of the bond (Z_π) and the formation energy of aromatic hydrocarbons are calculated. In the case of the latter data were taken from the book by V. M. Tatevskiy (Ref 12) and

An Electron Model of the Chemical Structure of Molecules. II

the change of the kinetic energy was explained according to the Heisenberg (Geyzenberg) principle. There are 4 tables and 14 references, 11 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Institute of Physical Chemistry imeni L. Ya. Karpov)

SUBMITTED: January 30, 1957

SOV/2o-12o-6-21/59

AUTHORS: Shigorin, D. N., Shcheglova, N. A., Nurmukhametov, R. N., Dokunikhin, N. S.

TITLE: The Effects of the Position and of the Nature of the Substituent on the Fluorescence Spectra of Anthraquinone Derivatives in Frozen Solutions(Vliyaniye polozheniya i prirody zamestitelya na spektry fluorestsentsii proizvodnykh antrakhinona v zamorozhennykh rastvorakh)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 12o, Nr 6, pp. 1242 - 1245 (USSR)

ABSTRACT: First a survey of previous papers and of the present state of the problem under review is given. This is a study of the fluorescence of much diluted solutions (C = 10-4 to 10-5mol/l) of anthraquinone and of its derivatives at 77°K. n-heptane, n-hexane and n-octane served as a solvent. The spectra were excites by a group of mercury lines. A fine structure of the oscillations was found in the fluorescence spectra of anthraquinone, of its β-derivatives (β-Cl-anthraquinone, β-methyl anthraquinone, β-amino anthraquinone) and of anthrone. The spectrum exhibited by anthraquinone in different solvents remains

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the same. It has 24 - 28 lines and shows a complicated structure. The spectrum of anthraquinone apparently is divided into several parts by the most intensive electron oscillation bands. The shape of the spectrum is repeated in each of these parts. These principal bands are divided into several components. When hexane is used instead of octane the number of components and the nature of the splitting-up is changed, the position of the bands and the distances between them are maintained. The principal form of the spectrum is maintained in the spectra of all compounds with a fine structure. It exhibits a three times repeated picture in the ranges between the intensive bands. The spectra of the α derivatives of anthraquinone are markedly shifted towards red as compared to the spectra reviewed above. They appear in the form of rather washed-out bands. The spectrum of β-oxy anthraquinone also consists of washed-out bands and is shifted towards red. The evidence advanced substantiates the hypotheses concerning the influence of the position of the substituent and of its nature upon the fluorescence spectra of the molecules under consideration.

The Effects of the Position and of the Nature of the Substituent on the Fluorescence Spectra of Anthraquinone Derivatives in Frozen Solutions SOV/20-120-6-21/59

There are 2 figures, 1 table, and 7 references, which are Soviet.

PRESENTED: March 27, 1958, by A. N. Terenin, Member, Academy of Sciences, USSR

SUBMITTED: March 21, 1958

1. Anthracene sclutions--Fluorescence 2. Anthracenes--Spectra
3. Anthracenes--Structural analysis

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5(2,3)
AUTHORS: Rodionov, A. N., Shigorin, D. N., SOV/20-123-1-30/56
Talalayeva, T. V., Kocheshkov, K. A., Corresponding Member, Academy of Sciences, USSR

TITLE: Infrared Spectra of Organolithium Compounds (Infrakrasnyye spektry litiyorganicheskikh soyedineniy) Intermolecular Lithium Bond (Mezhmolekulyarnaya litiyevaya svyaz')

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 1, pp 113 - 116 (USSR)

ABSTRACT: The investigated absorption spectra were taken from the mentioned compounds of type Alk-Li and Ar-Li. In particular, methyl-, ethyl-, butyl-, dodecyl-, phenyl-, p-and o-tolyl as well as α-naphthyl lithium were studied. They were prepared and isolated according to a method previously described (Refs 1,2). In the spectrum of methyl lithium (Fig 1), 6 main frequencies are recorded, corresponding with the oscillation theory of this kind of molecules. The band with the frequency 1052 cm^{-1} is assigned to the valence oscillation of the group

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Infrared Spectra of Organolithium Compounds. Intermolecular Lithium Bond

$C^{-\delta} - Li^{+\delta}$. The accuracy of this assignment is in accordance with the spectral analysis of ethyl-, butyl-, and dodecyl lithium. Thus, the frequency of the valence oscillation, being $\sim 1050\ cm^{-1}$, is specific for the respective series of compounds. Further proof of this fact is presented. The variation of the mentioned frequency of the C-Li group on the transition from the vaporous state to the solid and to solutions is apparently related to the fact that the C-Li groups in crystals and solutions take part in some intermolecular reactions. This in particular is shifting the C-Li-band in the direction of the long waves. Thus, the spectra show definitely that the molecules of the organolithium compounds in crystals and solutions are associated under complex formation (in conformity w th the references 3-8). If in the crystals the existence of chains is possible, in solutions with non-polar solvents the formation of associates under reduction of the entire dipole interaction is more favorable. This can be attained by

Infrared Spectra of Organolithium Compounds. Intermolecular Lithium Bond

the formation of various cycles as well as by variation of character and length of the chain. It is possible that different types of associates are existing in the solutions which are passing into one another on dilution, heating and under the influence of light in an atmosphere of nitrogen(in accordance with the results of cryoscopy ,References 4, 6-8). In the solutions of ethyl lithium in hexane, cyclohexane, and cyclohexene the portion of those molecules which do not take part in the association is larger than the portion of molecules associated . The type of association in the mentioned solvents is different from that in aromatic hydrocarbons. The spectra are given in figure 3. Extent and character of association of the molecules R-Li have to depend in the respective solutions to a considerable extent upon the length of the carbon chain. With a prolongation of the chain the probability of the formation of cyclic associates might decrease, whereas the possibility of a formation of the linear complexes must increase.

An exception is methyl lithium. Apparently, the variation of the character and degree of association of the R-Li molecules greatly affects the dipole moment, according to the nature of the compound, the concentration and the temperature. It can be assumed that the dipole moment of ethyl lithium is approaching the dipole moment of a free molecule in dilute hexane solutions (as confirmed by common studies with V.N. Vasil'yeva). The authors have found that benzene does not participate directly in the association of ethyl lithium. According to the results the authors concluded that associations of organolithium compounds by an intermolecular lithium linkage are existing. Finally, cases of such interactions are discussed. There are 3 figures and 10 references, 3 of which are Soviet.

SUBMITTED: July 5, 1958

Card 4/4

SHIGORIN, D. N.; SHCHEGLOVA, N. A.; and NURMUKHAMETOV, R. N.

"Fluorescence Spectra of Anthraquinone and its Derivatives in Frozen Solutions."

report presented at the 4th International Meeting of Molecular Spectroscopy, Bologna, Italy, 7-12 Sept 1959.

Institute of Physical Chemistry, the University, Moscow.

5(3) SOV/62-59-4-20/42

AUTHORS: Shemyakin, M. M., Shigorin, D. N., Shchukina, L. A., Semkin, Ye. P.

TITLE: Structure and Mechanism of the Hydrolytic Splitting of α-Nitro-α-Phenylacetophenon o-Carboxylic Acid (Stroyeniye i mekhanizm gidroliticheskogo rasshchepleniya α-nitro-α-fenil-atsetofenon-o-karbonovoy kisloty)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 695-698 (USSR)

ABSTRACT: To determine the structure of α-nitro-α-phenylacetophenone-o-carboxylic acid and its salts the spectra of these compounds were investigated in the present work (Table 1). These investigations have provided an answer to the question relating to their structure and their different behavior in the presence of hydrolyzing agents. As was to be expected, α-nitro-α-phenylacetophenone-o-carboxylic acid, like other aromatic o-aldehyde-(keto)-acids, has the structure of lactol (IIIb) rather than that of the keto acid (IV) in the crystalline state as well as in solution. After the actual structure of the α-nitro-α-phenylacetophenonic acid and of its disodium salt had been clarified, its different behavior in the

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Structure and Mechanism of the Hydrolytic Splitting of α-Nitro-α-Phenylacetophenon -o-Carboxylic Acid SOV/62-59-4-20/42

presence of hydrolyzing agents has been understood. As was shown before (Ref 3) the C—C bonds can split in those compounds in which a prototropic group (V) is present or can be formed in the molecule. The tendency to split depends directly on the degree of polarization of the C—C bond under the action of the substituent. α-Nitro-dinitrophenylacetophenone-o-carboxylic acid itself, having a lactol (IIIb) structure, does not only contain the required group (V) but also a nitro group which can polarize the splitting bond to a very high degree in the required direction. For this very reason the acid (IIIb) splits easily to form phthalic acid anhydride and phenylnitromethane if the pH-value of the solution exceeds 7. In the molecule of the disodium salt, on the other hand, the prototropic group (V) is not contained nor can it be formed by hydration owing to the structure of this salt. This fact is responsible for the resistance of this compound to hydrolytic splitting. There are 1 table and 11 references, 8 of which are Soviet.

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Structure and Mechanism of the Hydrolytic Splitting of α-Nitro-α-Phenylacetophenon -o-Carboxylic Acid SOV/62-59-4-20/42

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences, USSR)

SUBMITTED: July 13, 1957

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SOV/48-23-1-8/36

24(7)
AUTHORS: Shigorin, D. N., Shcheglova, N. A., Nurmukhametov, R. N.

TITLE: Influence of the Position and Nature of the Substituent Upon the Fluorescence Spectrum of Anthraquinone Derivatives in Frozen Solutions (Vliyaniye polozheniya i prirody zamestitelya na spektry fluorestsentsii proizvodnykh antrakhinona v zamorozhennykh rastvorakh)

PERIODICAL: Izvestiya Akademii nauk SSSR. Seriya fizicheskaya, 1959, Vol 23, Nr 1, pp 37 - 39 (USSR)

ABSTRACT: In the present paper the authors studied the fluorescence spectra of strongly dilute solutions of anthraquinone and its derivatives at 77°K. n-hexane, n-heptane and n-octane were used as solvents. The spectrum investigations were carried out according to the method described by Shpol'skiy (Ref 1). The oscillation microstructures of the fluorescence spectra of anthraquinone and its β-derivatives: β-chloro, β-methyl and β-amino anthraquinone were considered. The anthraquinone spectrum covers a few intense principal bands which reappear in each spectrum. Each band is split into several components. On the transition from hexane to octane, the number of components and way of distribution vary,

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whereas the position of the bands is maintained. It was observed that all spectra tend toward equalizing the intensity of the components of the central bands during the shift toward the long-wave range. The components of the intense bands correspond to the completely symmetrical C=O oscillation in the ground state of electrons. The nature of distribution of the electron-vibration level is connected with the orientation of fluorescent molecules in the crystal lattice of the solvent and has hitherto been investigated insufficiently. The α-derivatives of anthraquinone yield different spectra. Within the red range they are shifted to a large extent and their bands are indistinct. The authors investigated the spectra of α-oxy anthraquinone, α-chloro anthraquinone, 1,5-dioxy anthraquinone, 1,8-dioxy anthraquinone, 1,4-dioxy-anthraquinone and β-oxy anthraquinone. The latter β-derivative belongs also to this group because of its hydrogen bond that is produced in weak concentrations. This hydrogen bond renders the spectra of the α-derivatives of anthra-

quinone indistinct. It always occurs in such cases where an interaction between the substituents OH or NH_2 and the C=O group is possible. The data obtained on the fluorescence of frozen solutions of anthraquinone and its derivatives are parallel to those mentioned by Karyakin and Terenin (Ref 3) on the investigations of fluorescence extinction by oxygen as well as to the changes in the electronic and infrared absorption spectra of anthraquinone derivatives. There are 4 figures, 1 table and 4 Soviet references.